Pesticide Concentrations in the Don and Humber River Watersheds
(1998 – 2000)

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Pesticide Concentrations in the Don and Humber River Watersheds (1998-2000)

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Abstract and Summary

In 1998, a study of the Don and Humber River watersheds was initiated to investigate the potential for surface water contamination from the use of lawn care pesticides and fertilizers. Surface water samples were collected and tested for nutrients, phenoxy acid herbicides, triazine herbicides, organophosphorus insecticides, and other pesticides associated with lawn care use. Samples were collected from several sites in the Don and Humber River watersheds during base flow periods and runoff events each year from 1998 through 2000.

Nine pesticides and a metabolite were detected in surface waters of the Don and Humber Rivers; samples were analyzed for up to 159 pesticides. The Canadian Water Quality Guideline for the Protection of Aquatic Life for carbofuran was exceeded once in 133 samples. The Ontario Water Quality Objective for the Protection of Aquatic Life for diazinon was exceeded in 20% of the samples taken. All other pesticides detected were below available water quality guidelines. Nutrients such as total phosphorus, nitrate and ammonia were detected. Total phosphorus was frequently detected over the Ontario Interim Provincial Water Quality Objective.

1.0 Introduction

The objective of the study was to determine whether the pesticides and fertilizers used on urban lawns in the City of Toronto could be measured in surface waters of the Don and Humber Rivers, and in some of their tributaries, to attempt to determine spatial and temporal trends in concentrations and to identify possible environmental concerns by comparing ambient concentrations to available federal and provincial water quality criteria. In addition, samples were taken from a number of locations in a small tributary which flowed through a municipal golf course and into the Humber River to determine whether golf course turf care contributed to pesticide loadings. This is an interim report. A final report will be published in 2003 which will include data collected in 2001. Interested readers can contact the primary authors (john.struger@ec.gc.ca or tim.fletcher@ene.gov.on.ca) to obtain the final report.

Due to a greater awareness of environmental issues, public concern has grown recently regarding the use of pesticides and fertilizers, particularly in urban environments. While, based on total kilograms applied, agricultural pesticide use is greater than urban pesticide use, urban applications are still significant (Hoffman et al. 2000). However, there is a lack of data on the presence of pesticides in urban streams.

Prior to the mid-1970's, organochlorine chemicals such as DDT and chlordane were used for pest control. These chemicals have very low water solubility, a high affinity for sediment and biota, and a potential to bioaccumulate in fish, and their use has subsequently been banned. Modern lawn care pesticides are generally non-persistent and non-bioaccumulating. However, these chemicals are generally very water soluble and have a low affinity for sediment, so they remain in the water column where they may affect aquatic organisms.

In 1994, the Ontario Ministry of Agriculture Food and Rural Affairs (OMAFRA) published the results of their 1993 Pesticide Use Survey. This also included professional lawncare applicators. The total amount of active ingredients used in Ontario were estimated. Table 1 lists the ten pesticides used most frequently by professional lawncare applicators in the province for 1993, and the percentage that each active ingredient comprises of the estimated total amount of active ingredients used. These ten chemicals accounted for approximately 95% of the total amount of active ingredients estimated to be applied by lawn care

applicators. According to the survey responses, approximately 60% of the total amount of active ingredient used by professional applicators was applied to residential lawns (OMAFRA 1994).

Active Ingredient	% of total reported use
Mecoprop	19.34
2,4-D	17.28
Dicamba	14.61
Diazinon	9.80
Chlorpyrifos	9.66
2,4-DB	7.82
Dichlorprop	8.04
MCPA	3.72
Bacillus thuriengensis	3.08
Glyphosate	1.43

Table 1: Active Ingredients most frequently used by professional applicators in Ontario (from OMAFRA 1994)

In urban areas such as Toronto, stormwater inputs usually are discharged directly through overland runoff or indirectly through the storm sewer network to urban streams or rivers such as the Don and Humber Rivers. Subsequently, there may be a risk to aquatic biota from these in-use pesticides because of the proximity of lawns in urban areas to stormwater drainage systems. Stormwater inputs of these pesticides would be expected to be at their highest during runoff events occurring immediately following their application. Typically there are three periods (ie. spring, summer and fall) when pesticides are applied to lawns.

There have been a number of surveys investigating the use of pesticides on residential lawns. A 1994 survey of homeowners in Guelph, Ontario found that 60% of homeowners applied pesticides to their lawns, half of whom applied it themselves while the rest employed a lawn care service (Struger et al. 1994). This survey found twenty-two different insecticides and herbicides were used on lawns in the two storm water catchment areas under study. The authors also reported that application rates were higher for products used by lawn care companies compared to those used by individual homeowners.

In 2000, the City of Waterloo polled residents of the city on their use of pesticides and fertilizers on lawns, as well as their perspectives towards the use of lawn care pesticides. Residents were placed in one of four categories based on their perspective towards pesticide use; Not Concerned (16%), Mixed Feelings (41%), Guilt (19%) and Conscious Objectors (24%). When asked whether they had applied a weed control product at least once in the previous year, over 40% of those considered Conscious Objectors indicated they had while over 80% of those identified in the Guilt category had done so. Approximately 60 to 70% of those identified as Not Concerned about pesticide use and those with Mixed Feelings indicated they had used a weed control product. When asked whether they had applied an insect control pesticide at least once in the last year, only 20% of Conscious Objectors indicated they had, while use by the other segments were much higher, ranging from approximately 55% for those that were Not Concerned about pesticide use, to approximately 80% of those identified in the Guilt category (City of Waterloo, unpublished). In total, approximately 70% of those polled indicated they had used a weed control product at least once in the previous year, while approximately 60% indicated they had used an insect control product over the same time period.

In 2001, the Toronto Public Health Department conducted a similar survey. They polled 341 households which had lawns. More than half (55%) of householders reported that no pesticides were applied to their lawns in the previous two years. For those homeowners that indicated pesticides were applied, more than half applied the pesticides themselves rather than hiring a professional. Homeowners with larger lawns were more likely to hire a professional applicator (TPHD, 2002).

An Ipsos-Reid poll conducted in 2001 surveyed 600 Canadians (non-condominium owners) on their perspectives towards pesticide use. Approximately 49% of those polled indicated that they would use chemical products themselves to control pest problems, while 13% indicated they would hire a professional (CMCS, unpublished).

Figure 1: Location of Don River Watershed Sampling Stations

Overall, these homeowner surveys indicate that there is a relatively even split between those that treat lawns and those that do not. Some variability in pesticide use from city to city is expected, especially in those municipalities where there has been a high level of promotion of pesticide use reduction (e.g. Waterloo and Toronto).

2.0 Methods

2.1 Field Sampling

Individual grab water samples were collected during rain events (wet events) and during base low periods (dry events) at sampling locations from April to December in 1998, from March to November in 1999, and from August to November in 2000 (Figures 1 and 2, Station numbers identified in Table 2).

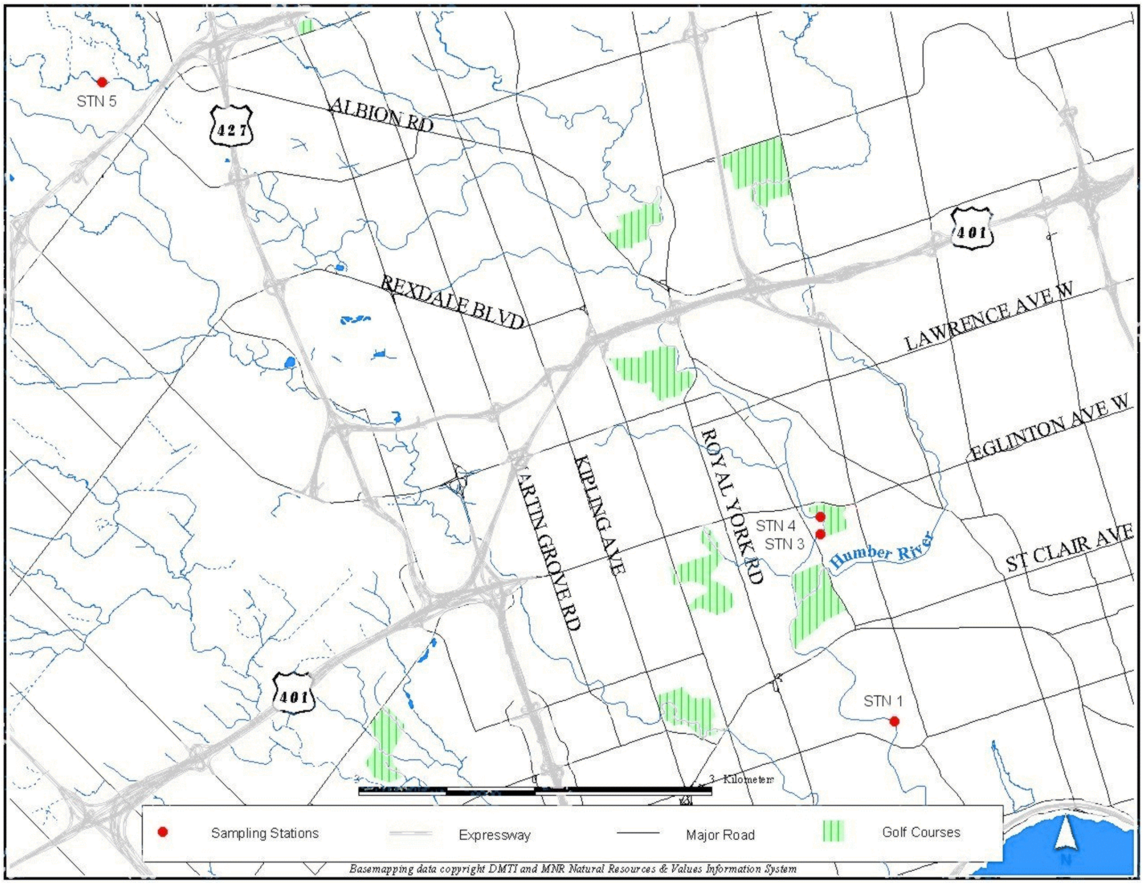

Figure 2: Location of Humber River Watershed Sampling Stations

In 1998 through 2000, water samples were collected at the mouths of the Don and Humber Rivers, Wilket Creek in the Don River watershed, and at three locations on a tributary of the Humber River flowing through the municipally operated Scarlett Woods Golf Course. In 1999, two sites, the West Don River at Steeles Avenue and the West Humber River at Gorewood Drive were added. Sampling at these sites would

determine the pesticide concentrations present in rivers entering the City of Toronto and, when compared to the concentrations at the Don and Humber River mouths, should indicate pesticides introduced in the urbanized Toronto area. In 2000, a site on Burke's Brook in Sherwood Park on the Don River watershed was added.

The number of samples collected and corresponding weather is presented in Table 2. In total, 133 samples were taken from 1998 to 2000, 57 wet events and 76 dry events. The stations most frequently sampled during the study were at the mouths of the Humber and Don Rivers.

When possible, wet event samples were collected a short time after the start of the precipitation events in order to catch the first flush conditions, or during the peak flow periods (See Figure 3). At these times the greatest pesticide run-off is expected to occur.

The surface water samples were collected by gloved hand in washed glass bottles (U of G SOP# 955-013-AMSCO470 Washer) from mid-stream and, where possible, at 10 to 15 cm below the surface. Three or four 1-L surface water samples were collected for pesticide analyses at each site. Samples were kept in coolers in the field and were refrigerated in the lab before analysis. The samples were analyzed for total phosphorus (P), nitrate (NO3), ammonia (NH3), triazine herbicides, phenoxy acid herbicides, organophosphorus insecticides, organochlorine pesticides, carbamate fungicides, dithiocarbamate fungicides and other pesticides.

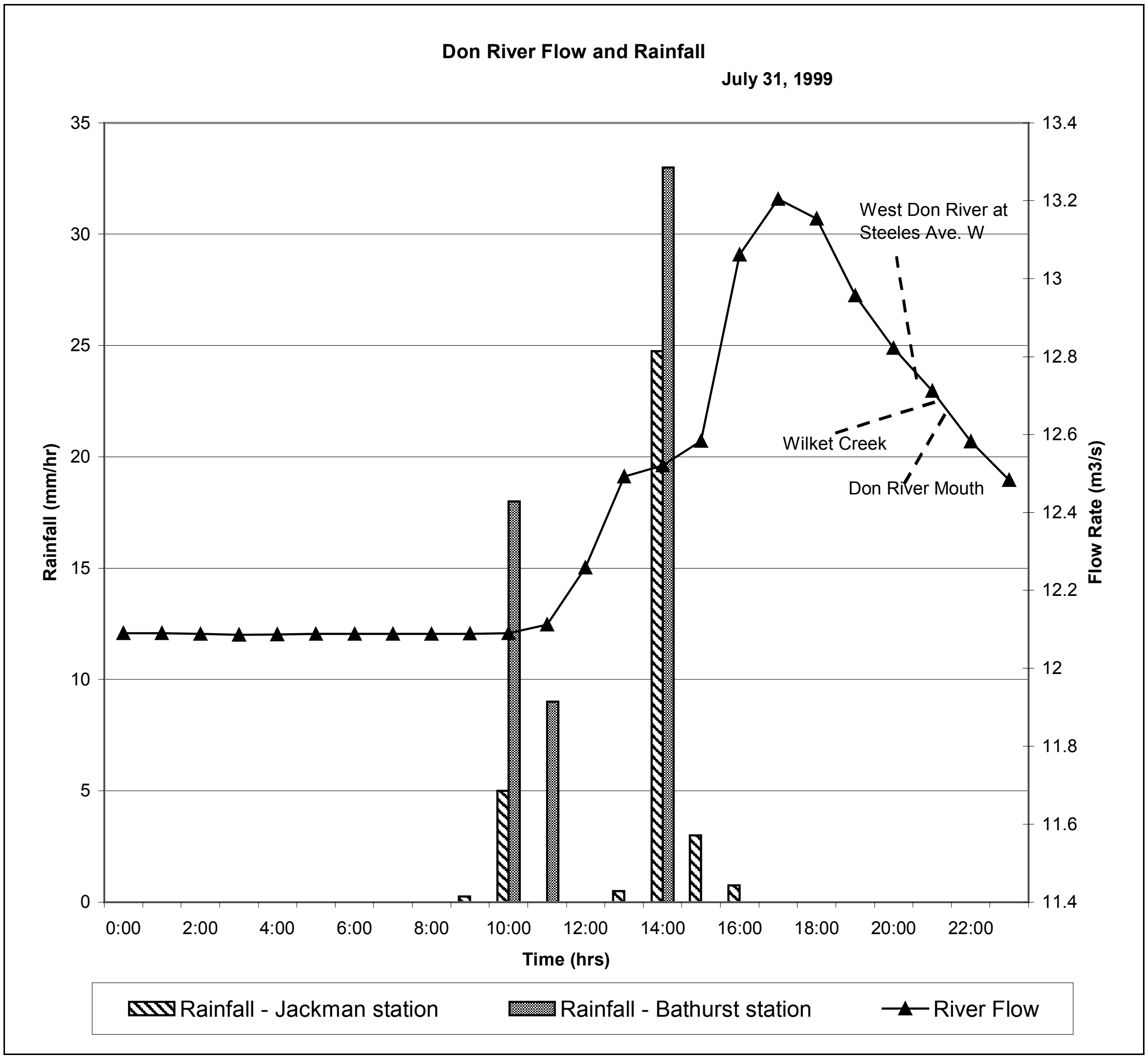

Figure 3: Example of wet event sampling times in relation to streamflow and rainfall at three locations on the Don River. Site indicators show when samples were taken.

2.2 Analytical Methodology

2.2.1 Nutrients

Nutrient analyses were carried out at the City of Toronto's Wastewater Quality Laboratory, Works and Emergency Services Department. The methodologies used for all nutrients are from APHA (1998) and each one is identified by its reference number.

Phosphorus (P) [4500-P E]: Phosphorus in the sample is converted through acid hydrolysis to the soluble orthophosphate. Ammonium molybdate and potassium antimonyl tartrate react in acid medium with the soluble phosphate to form a complex that is reduced to a dark blue species with ascorbic acid. The phosphate is then determined colorimetrically.

Nitrate (NO3) [4110-C]: A small portion of a filtered, homogenous, aqueous sample is injected into an ion chromatograph. Anions are separated by their affinity on the active sites of the column packing material. Conductivity detector readings are used to compute concentrations.

Ammonia (NH3) [4500-NH3-G]: The sample is determined colorimetrically on a Technicon automated analyzer. The ammonia reacts with alkaline phenol and sodium hypochlorite in a buffered solution to form indophenol blue. Sodium nitroprusside is added to enhance the sensitivity. The absorbance of the resulting

indophenol blue is measured at 630 nm wavelength and from this measurement the ammonia concentration is determined.

2.2.2 Pesticides

Surface water samples were analyzed by the University of Guelph's Laboratory Services Division. All analytical methods, except the one for imidacloprid, have been accredited through the Standards Council of Canada/ Canadian Association of Environmental Analytical Laboratories (SCC-CAEAL) partnership. One hundred and fifty-nine pesticides (herbicides, insecticides and fungicides) and some of their metabolites were analyzed (Appendix 1) and were determined by the following methods. Many of the analytical methods used detect a series of related pesticides (e.g. organophosphorus, organochlorine), thus the large number of pesticides analyzed for. The focus of this study was on pesticides commonly used in lawncare (as indicated in Appendix 1). Except for *Bacillus thuriengensis* (a biological pesticide), all of the most frequently applied pesticides (Table 1) were monitored for. There were slight differences in types of pesticides analyzed in 2000, compared to 1998 and 1999 in order to add specific lawncare pesticides of interest.

Laboratory recoveries for the various classes of pesticides were within the acceptable range. Laboratory blanks demonstrated that the system was free from internal contamination. Duplicate field samples and field blanks were collected and did not indicate any significant problems.

Organophosphorus Insecticides, Organonitrogen Pesticides, Organochlorine Pesticides, Carbamate Insecticides, Triazine Herbicides, and Imidacloprid Determination

Water samples (1L) were extracted twice with 100 ml of dichloromethane by shaking for one minute after the addition of 50 ml of aqueous saturated sodium chloride solution. The extracts were dried with anhydrous sodium sulphate and evaporated just to dryness. The residual material was re-dissolved in 5.0 ml of hexane. The organophosphorus insecticides, organochlorine pesticides, carbamate insecticides, triazine herbicides and organonitrogen pesticides were analyzed using a capillary column gas chromatograph equipped with a nitrogen phosphorus detector. An extra florasil cleanup step was used in the extraction process for organochlorine pesticides. Imidacloprid was analyzed using high performance liquid chromatography with an ultra-violet detector.

The method detection limit (MDL, as defined by USEPA 1997) for most of the organophosphorus insecticides and for triazine herbicides was 0.05 ug/L, for organonitrogen, organochlorine and carbamate pesticides the MDL was 0.1 ug/L, and for imidacloprid the MDL was 1.0 ug/L. For diazinon and atrazine the MDL was 0.02 ug/L.

Table 2: Number of samples taken during wet and dry events, 1998-2000.

Sampling Site	Station Number	1998		1999		2000		Total	
		Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
Don River Mouth	STN9	2	2	9	6	2	6	13	14
West Don River	STN6	-	-	6	3	1	3	7	6
Wilket Creek	STN7	1	2	4	6	1	3	6	11
Humber River Mouth	STN1	2	2	9	6	2	6	13	14
West Humber River	STN5	-	-	6	3	1	3	7	6
Scarlett Woods GC #1	STN4	0	2	4	6	1	3	5	11
Scarlett Woods GC #4	STN3	0	2	4	6	1	3	5	11
Burke's Brook	STN8	-	-	-	-	1	3	1	3
Total		5	10	42	36	10	30	57	76

Glyphosate Determination
A 20 ml aliquot of the water sample was evaporated to dryness and reconstituted in 1.0 ml of the mobile phase solvent(s). This extract was examined using high performance liquid chromatography (HPLC) with a Post Column Reaction System and flourescence detection to determine glyphosate and its metabolite AMPA. The MDL for both glyphosate and AMPA was 0.05 ug/ml (50 ug/L).

Phenoxy Acid Herbicide and Dithiopyr Determination

An 800 ml aliquot of the water sample was acidified using ^{18}N H_2SO_4 and extracted with 90 ml of ethyl acetate by tumbling for 1 hour using a tumbler apparatus. After tumbling, the contents were extracted with an additional 25 ml of ethyl acetate and the combined extracts were dried with anhydrous sodium sulphate. Two (2.0) ml of 2,2,4-trimethylpentane was added, and evaporated to almost dryness. This extract was redissolved in 8.0 ml of ethyl acetate. Four (4.0) ml was removed for dithiopyr analysis and the remaining 4.0 ml was evaporated and derivatized by adding 3.0 ml of diazomethane to the extract and letting it stand for 30 minutes. The contents were then evaporated just to dryness using a pure nitrogen stream. The residual material was re-dissolved in 2.0 ml of 2,2,4-trimethylpentane for phenoxy acid herbicide analysis. The phenoxy acid herbicide and dithiopyr residues were determined separately using capillary column gas chromatography with a mass selective detector (GC-MSD). The MDL was 0.1 ug/L for the phenoxy acid herbicides while for dithiopyr the MDL was 10 ug/L.

Ethylenebisdithiocarbamate (EBDC) and Dimethyldithiocarbamate Fungicide Determination

Dithiocarbamate was decomposed with hot mineral acid and stannous chloride to form an amine and carbon disulphide. The gases were drawn through two adsorption traps. The first trap contained NaOH and benzene to capture any hydrogen sulphide formed. The second trap contained Cullen's chromogenic reagent to react with any carbon disulphide generated and form a coloured complex. The absorption was measured spectrophotometrically at 435 nm. The MDL was 5 ug/L. This method is suitable for the determination of total dithiocarbamates, as EBDC equivalent carbon disulphide (CS_2), in various substrates, including water, soil, fruit, and vegetables.

3.0 Results and Discussion

The Don and Humber Rivers are the two largest of six watersheds that drain the City of Toronto and surrounding areas. Both have headwaters above the city, in rural areas. By 1993, approximately 80% of the

Table 3. Summary of surface water pesticide monitoring results (1998-2000). Table provides summary results for those pesticides detected in samples

Pesticide	Water Quality Guideline/ Objective	Detection Limit ug/L	Maximum Concentration (ug/L)	Frequency of Detection (% of samples)	Frequency of Guideline/ Objective Exceedence (% of samples)
diazinon	0.08 ug/L*	0.02	1.00	29	20
cypermethrin	-	0.05	0.38	0.7	-
atrazine	1.8 ug/L**	0.02	1.1	3.7	0
des-ethyl atrazine	-	0.05	1.7	0.5	-
metolachlor	7.8 ug/L**	0.1	2.0	2	0
MCPP	4 ug/L**	0.1	1.77	30	0
2,4-D	4 ug/L**	0.1	2.1	6.6	0
carbofuran	1.8 ug/L**	0.1	3.0	1.5	0.7
dicamba	10 ug/L**	0.1	0.27	1.5	0
metribuzin	1 ug/L**	0.05	0.12	0.7	0

*Ontario Water Quality Objective for the Protection of Aquatic Life (MOE 1994)
** Canadian Water Quality Guidelines for the Protection of Aquatic Life (CCME 1999)

Don River watershed was urbanized, with the other 20% remaining agricultural (MTRCA). In 1995, approximately 45 % of the Humber River watershed was urban or urbanizing (especially in the municipalities of Aurora, Brampton, Richmond Hill, and Vaughan) and 55% of the watershed remained rural. Today, the proportion of urbanized land of each watershed has grown even more. A significant amount (approximately 46%) of the land base remains in agricultural use for livestock and cash crops on the Oak Ridges Morraine, South Slope, and Peel Plain in the Towns of Caledon and Vaughan in King Township (CHRS 2001). Much of this area drains to the West Humber River.

3.1 Nutrients

Total phosphorus concentrations sampled during dry events, averaged at, or were just above the Interim Provincial Water Quality Objective (IPWQO, Ontario Ministry of the Environment, 1994) of 0.03 mg/L on both watersheds. Phosphorus concentrations above the interim guideline can result in excessive plant growth and possible eutrophication. Dry event concentrations in the tributary running through the Scarlett Woods Golf Course (SWGC) were about three to four-fold the IPWQO, however, the average concentrations entering the golf course (0.14 mg/L) exceeded those leaving it (0.10 mg/L) suggesting that the golf course does not contribute excessive phosphorous to the creek.

During rainfall conditions, the phosphorus concentrations in the main watercourses increased almost ten-fold compared to concentrations detected during dry conditions. While the elevated concentrations of phosphorus at the mouth of the Humber (Figure 4) and Don (Figure 5) Rivers may largely be due to Combined Sewer Overflow (CSO) inputs, sampling stations upstream of most CSO discharges on the Humber and Don, and samples from the small stream stations, also had higher concentrations.

Concentrations entering the City of Toronto around the Steeles Avenue boundary were slightly lower (0.19 mg/L on the Humber and 0.23 mg/L on the Don) than further down the urbanized reaches of the watersheds (0.4 mg/L on Humber at Eglinton Ave., and 0.65 mg/L at the Don River mouth). The highest

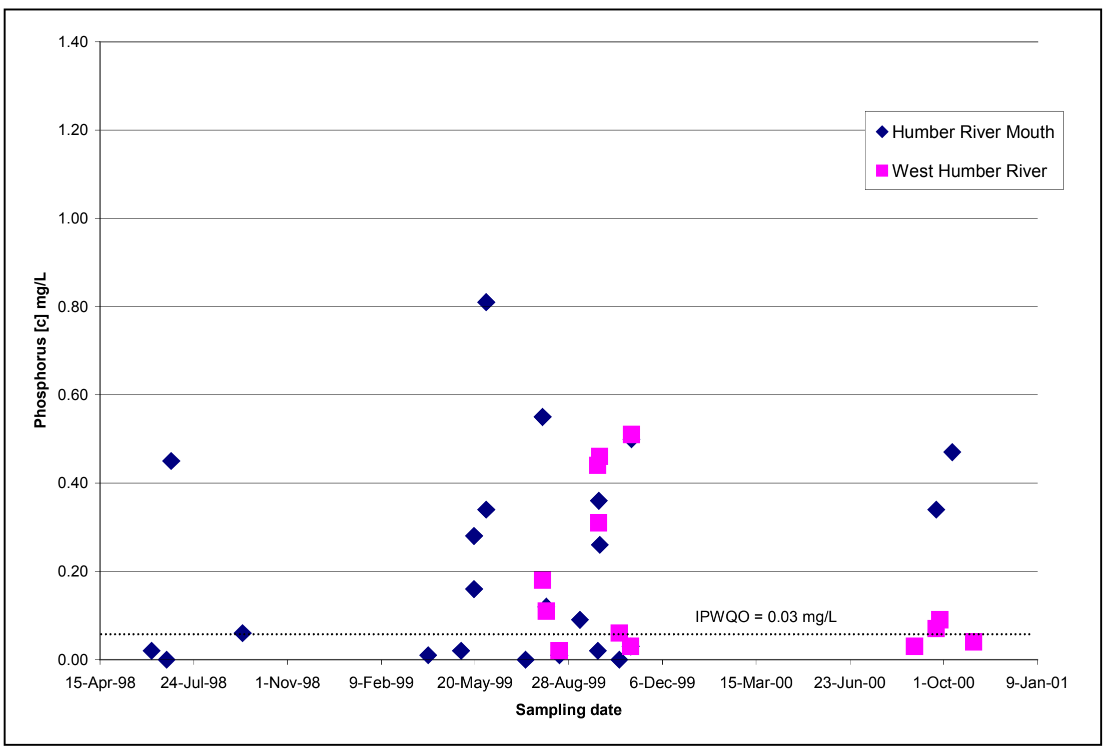

Figure 4: Phosphorus Concentrations in the Humber River

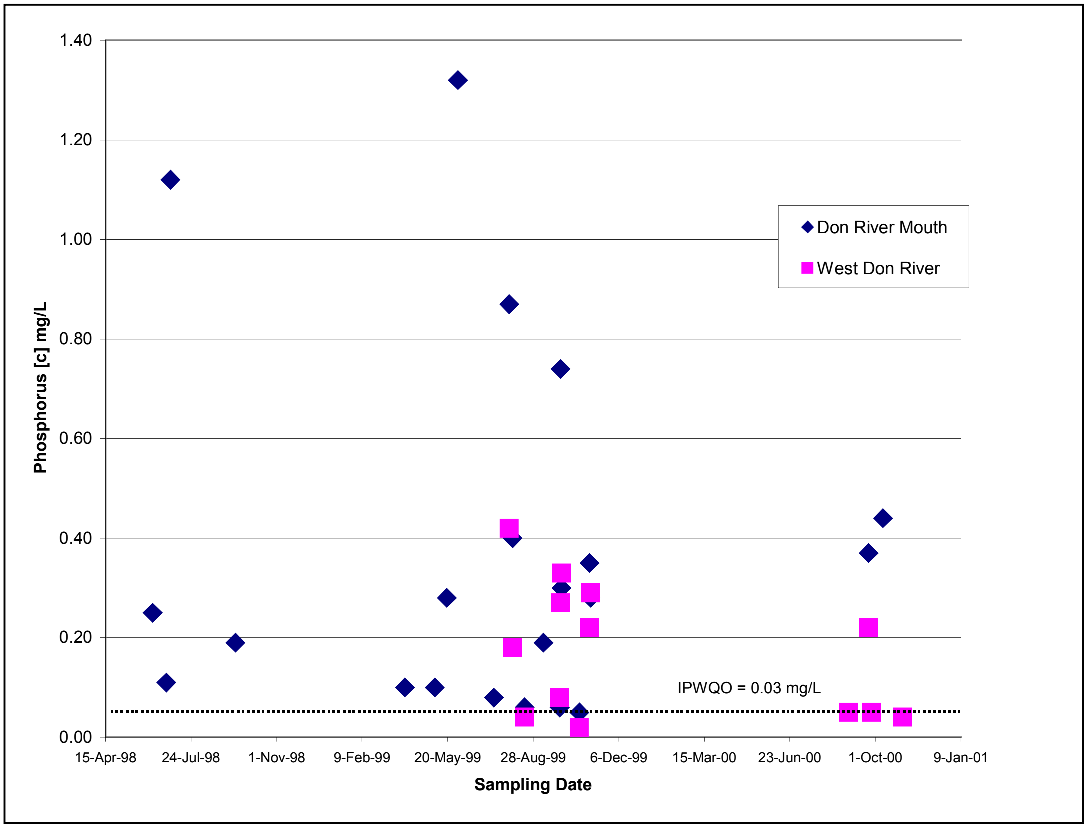

Figure 5: Phosphorus Concentrations in the Don River

phosphorus concentration was found at the mouth of the Don and is associated with the combined sewage overflow of the storm tanks from the North Toronto Sewage Treatment Plant during rainfall (max. 1.32 mg/L).

In contrast to the main watersheds, phosphorus concentrations merely doubled in wet event conditions over dry in the tributary running through the SWGC (Figure 6). Concentrations averaged a little more than half that of the main Humber River during rainfall.

Nitrate (NO_3) concentrations were quite variable during rain events and between the two watersheds. On the Don River watershed, concentrations were higher during dry weather conditions relative to wet. Conversely, on the Humber River watershed, the concentrations were higher during rainfall. There did not appear to be much difference between the concentrations of nitrate in the rivers entering the City, and the concentrations at the mouths. Typically, the nitrate concentrations in surface water were under 1 mg/L.

Typically, nitrate concentrations in Canadian lakes and rivers do not exceed 4 mg/L, however temperate streams and rivers draining agricultural areas in southern Ontario often exceeded these values (McNeely et al. 1979). Environment Canada has proposed an Interim Canadian Water Quality Guideline for nitrate of 13 mg/L based on the protection of amphibians (CCME 1999). Nitrate concentrations in this study never approached the proposed Interim CWQG.

Ammonia is the most reduced inorganic form of nitrogen in water. In the aquatic environment, mainly bacteria and blue-green algae reduce elemental nitrogen (N_2) to ammonia (NH_3) or ammonium ions (NH_4^+). Other groups of nitrifying bacteria convert ammonia to nitrite and nitrate. Ammonia is toxic to fish and high exposures cause an increase in gill ventilation hyperexcitability (suffocation), convulsions and death (Russo 1985). Effects of chronic exposure of fish to lower concentrations of ammonia include deleterious histological changes, a decrease in reproductive capacity, a decrease in growth and morphological development, and an increase in susceptibility to disease (Russo 1985). Ammonia concentrations tended to be higher during dry event sampling. Ammonia values ranged from non-detectable by laboratory methodology (ND) to 5.05 mg/L. Because the toxicity of un-ionized ammonia is affected by pH and temperature, the CWQG for the Protection of Aquatic Life (CCME 1999) set guidelines for total ammonia

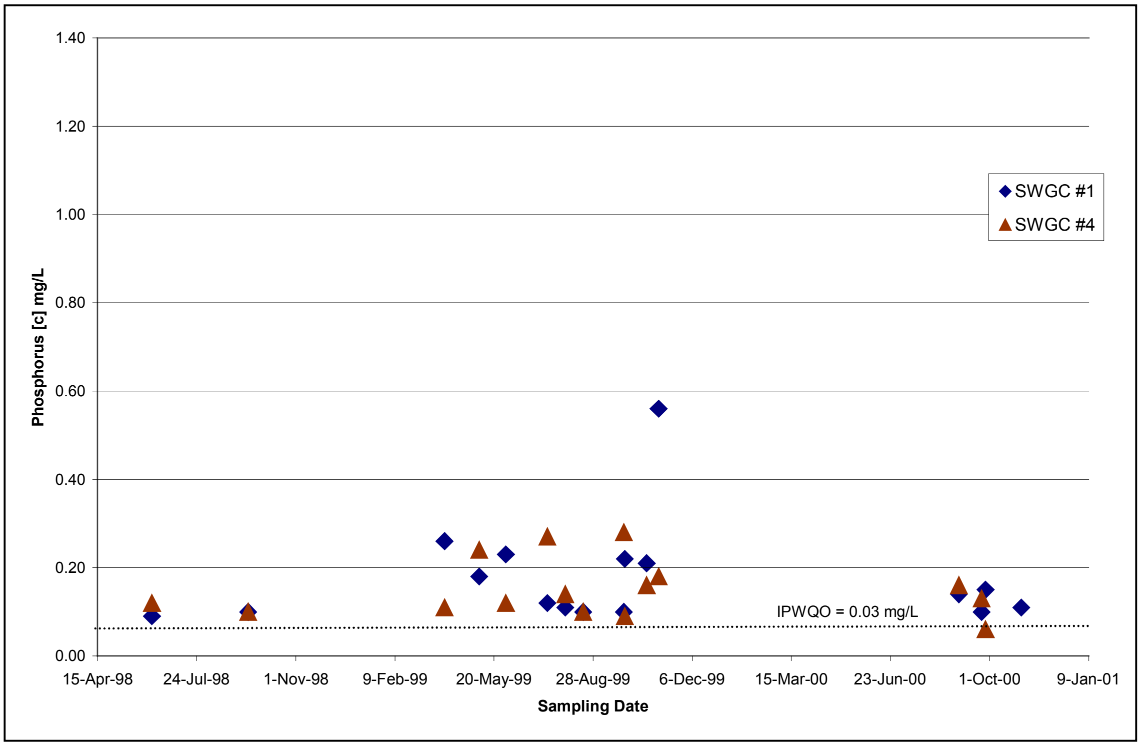

Figure 6: Phosphorus Concentrations along the Scarlett Woods Golf Course

that vary from 1.37 mg/L (pH 8.0 and temperature 10°C) to 2.2 mg/L (pH 6.5 and temperature 10°C). The CWQG was never exceeded at stations at the city limits, but was exceeded in approximately 10% of the samples from the Humber River mouth and approximately 40% of the samples from the Don River mouth (Figure 7). Ammonia can enter surface waters from several sources, including industrial wastes, sewage effluents, alternative fuel conversion processes, and agricultural discharges (Russo 1985). High ammonia concentrations may be a result of either the decomposition of nitrogenous organic matter such as animal or vegetable wastes or the microbial reduction of nitrates or nitrites under anaerobic conditions.

3.2 Pesticides

In 1998 and 1999, 155 active ingredients of pesticides were monitored from the following groups: organophosphorus, organochlorine and pyrethroid insecticides, and phenoxy acid and triazine herbicides. In 2000, organochlorine and pyrethroid insecticides were dropped from the analysis but three new active ingredients were added: glyphosate and its metabolite AMPA, imidacloprid, and dithiopyr. During the study 133 surface water samples were collected. Of the 159 pesticides that were monitored, nine pesticides and one pesticide metabolite were detected (Table 3). There was no detection of an organochlorine pesticide, EBDC fungicide or glyphosate. The compounds that were detected included: diazinon, cypermethrin, metolachlor, MCPP, 2,4-D, carbofuran, dicamba, metribuzin, atrazine and its metabolite, des-ethyl atrazine. Four of these pesticides (diazinon, 2,4-D, MCPP and dicamba) are commonly used for urban turf management, and are also used in agriculture.

The highest in-use pesticide concentration measured in the study was 3.0 ug/L of carbofuran (Table 3), which was nearly double the CWQG. Carbofuran was detected at the mouth of the Humber River and in Scarlett Woods Creek (Station 4), upstream of the golf course on the Humber River watershed. Since carbofuran is used exclusively in the agricultural sector, there is no explanation for its detection in the

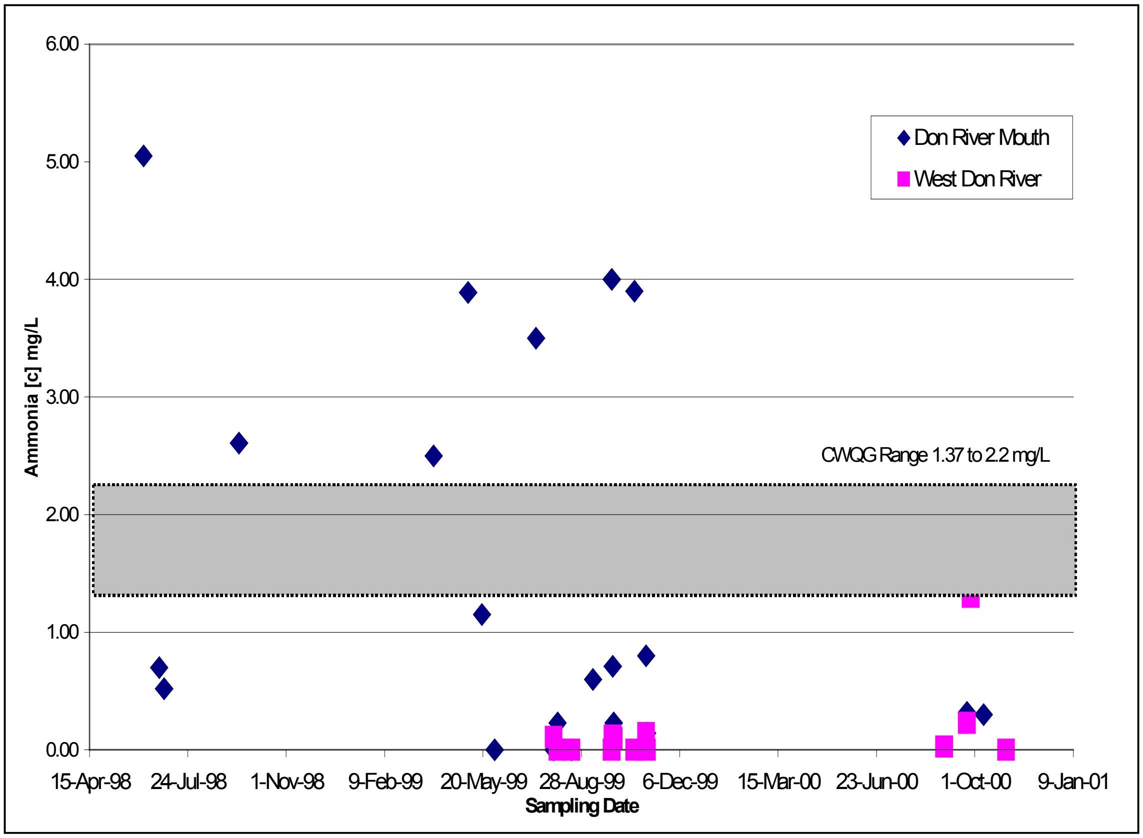

Figure 7: Ammonia Concentrations in the Don River

creek, which has no upstream agricultural lands. The most frequently detected pesticides were MCPP (detected in 30% of the samples), followed by diazinon (29%) and 2,4-D (6.6%). All three of these pesticides are commonly used for residential lawn-care, however there are also agricultural uses. All other compounds were detected less frequently; atrazine (3.7%), metolachlor (2.2 %), des-ethyl atrazine (1.5%), carbofuran (1.5 %),dicamba (1.5%), and cypermethrin (0.7%). Water Quality Guidelines/Objectives were exceeded for two of the pesticides (diazinon and carbofuran). In the case of carbofuran, the Canadian Water Quality Guideline for the Protection of Freshwater Aquatic Life (CCME 1999) was exceeded only once. For diazinon, the Ontario Water Quality Objective for the Protection of Freshwater Aquatic Life (OME 1994) was exceeded in approximately 20% of the samples taken. A greater number of pesticides were detected in samples from the Humber River than the Don River, perhaps as a result of more agricultural activity occurring in the upper part of the Humber watershed. This would explain the detection of atrazine only in the Humber River. A greater number of pesticides were detected at the mouths of the Don and Humber Rivers than at upstream sites (Table 4) which suggests that urban inputs of pesticides may contribute to the increased detections of these compounds. In general, most pesticides were detected more frequently at the river mouths compared to the city limits (e.g, diazinon). However, for both rivers, MCPP was detected more frequently at the city limits compared to the river mouths, possibly indicating that upstream agricultural use of this pesticide plays a significant role in MCPP contributions. There were more detections of pesticides in samples taken from the downstream site of the tributary running through the Scarlett Woods Golf Course (#4) than in samples collected from the tributary where it begins to enter the golf course (#1) [Tables 6].

Seven pesticides were detected in samples taken during wet events (Table 5). MCPP and diazinon were detected at seven sites and 2,4-D at four sites. Seven pesticides were detected at the mouth of the Humber River, followed by four pesticides at the mouth of the Don River, and three pesticides at Wilket Creek. At least two pesticides were detected at all of the sites. More pesticides were detected at the mouth of the Don

Table 4. Summary of surface water pesticide monitoring results at the mouth and city limit of the Don and Humber Rivers, (1998-2000).

Pesticide	Humber River				Don River			
	Mouth		City limits		Mouth		City limits	
	Max. Conc. (ug/L)	% samples with detections	Max. Conc. (ug/L)	% samples with detections	Max. Conc. (ug/L)	% samples with detections	Max. Conc. (ug/L)	% samples with detections
Diazinon	0.70	41	0.4	31	1.0	59	0.18	23
Cypermethrin	-	-	-	-	0.38	4	-	-
Atrazine	1.1	11	0.066	15	-	-	-	-
des-ethyl atrazine	1.0	4	-	-	-	-	-	-
Metolachlor	1.6	7	-	-	1.3	4	-	-
MCPP	1.0	33	1.0	39	1.1	41	1.0	54
2,4-D	1.0	11	1.0	8	1.1	11		
Dicamba	-	-	0.27	8	-	-	-	-
Metribuzin	0.12	4	-	-	-	-	-	-
Carbofuran	1.0	4	-	-	-	-	-	-

River than at the West Don River at Steeles Ave site during wet events. The same was true for the mouth of the Humber compared to the West Humber at Gorewood Drive site.

Six pesticides and one metabolite were detected in samples taken during dry events (Table 6). MCPP was detected at six of the eight sites, followed by diazinon at five sites and 2,4-D at three sites. Five pesticides were detected in the West Humber River, four pesticides and a metabolite were detected at the mouth of the Humber River followed by four pesticides at the mouth of the Don River and three pesticides and a metabolite at Wilket Creek. No pesticides were detected at the Scarlett Woods Golf Course site #1, or at Burke's Brook during dry events. There is some indication that an increase in pesticide detections may be related to the increased discharge to streams as a result of precipitation.

Diazinon concentrations in the Humber River tended to be higher during rain events, indicating that the run-off may play a role in contaminating the river. Figure 8 indicates that the highest concentration of diazinon in the Humber River watershed was detected at the Humber River mouth. Diazinon was more frequently detected at higher concentrations at the mouth of the Humber River, indicating that there is input from urban areas. This trend is more pronounced in the Don River Watershed (Figure 9). Diazinon concentrations were also higher at the mouth of the Don River compared to the upstream West Don River site at the City boundary. Diazinon was detected 2.5 times more frequently at the Don River mouth compared to the city limit site (Table 4). Concentrations of diazinon tended to be higher at the Don River mouth than the Humber River mouth, possibly due to the fact that the lands surrounding the Don River are more heavily urbanized than the area around the Humber River.

Although total phenoxy herbicide concentrations were well below the Canadian Water Quality Guideline for the Protection of Aquatic Life (i.e. 4 ug/L for 2,4-D, dicamba and MCPP) [CCME 1999], a similar trend to that observed for diazinon could be seen, with concentrations of phenoxy herbicides slightly higher at the mouth compared to the upstream sites (Figures 10, 11). There appeared to be little difference between concentrations of the phenoxy herbicides at the two river mouths (Table 9).

The results of this study suggest that stormwater drainage systems may be conveying nutrients and pesticides used on lawns in urban areas to the Don River and Humber River watersheds and ultimately, into Lake Ontario. Similar findings of contamination due to the residential use of pesticides has been reported in urban streams from various jurisdictions in North America. The United States Geological Service has

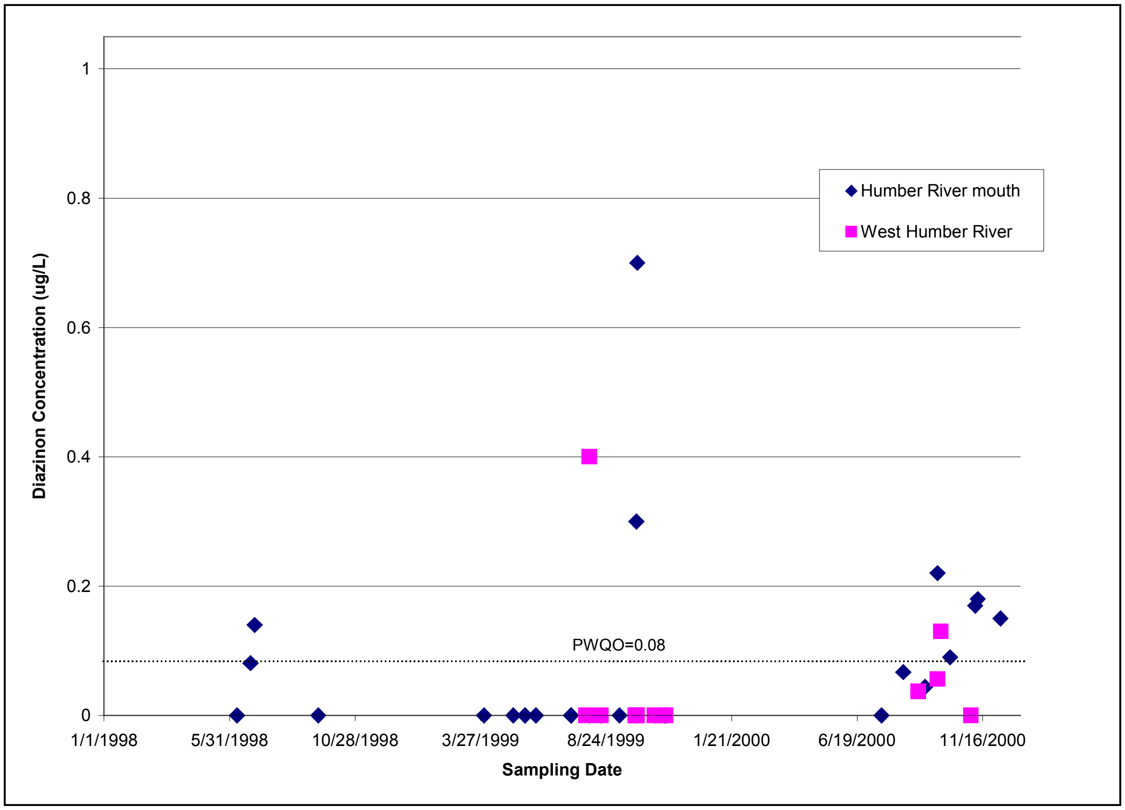

Figure 8: Diazinon Concentrations in the Humber River Watershed

documented widespread fertilizer, insecticide, and herbicide contamination of both surface waters and groundwaters of the continental United States (USGS 1999). The report documented that numerous streams were affected from the residential use of pesticides in urban areas. Insecticides were found more often, and usually at higher concentrations, in urban streams than in agricultural streams. Diazinon, carbaryl, chlorpyrifos and malathion were the most frequently detected insecticides. The herbicides most commonly found in urban streams were simazine, prometon, 2,4-D, diuron, tebuthiuron, atrazine and metolachlor. High inputs of nutrients such as phosphorus and nitrates were also observed in urban streams. Struger et al. (1994) has reported pesticide contamination of streams in the Region of Hamilton-Wentworth

Table 5. Summary of pesticides detected at Toronto sites during wet events (1998-2000).

Pesticide	Don River mouth	Humber River mouth	Scarlet Woods GC #1	Scarlet Woods GC #4	Wilket Creek	West Don River at Steeles Ave.	West Humber River at Gorewood Drive	Burke's Brook	Total # of Sites
diazinon	x	x		x	x	x	x	x	7
atrazine		x							1
metolachlor	x	x							2
MCPP	x	x	x		x	x	x	x	7
2,4-D	x	x		x	x				4
carbofuran		x	x						2
metribuzin		x							1
Total # of Pesticides (n=7)	4	7	2	2	3	2	2	2	24

Table 6. Summary of pesticides detected at Toronto sites during dry events (1998-2000).

Pesticide	Don River mouth	Humber River mouth	Scarlet Woods GC #1	Scarlet Woods GC #4	Wilket Creek	West Don River at Steeles Ave.	West Humber River at Gorewood Drive	Burke's Brook	Total # of Sites
diazinon	X	X			X	X	X		5
cypermethrin	X								1
atrazine		X					X		2
des ethyl atrazine		X			X				2
MCPP	X	X		X	X	X	X		6
Dicamba					X		X		2
2,4-D	X	X					X		3
Total # of Pesticides (n=7)	4	5	0	1	4	2	5	0	21

and two stormwater detention ponds in Guelph to be attributed to the residential use of pesticides. They found numerous detections of herbicides (e.g., 2,4-D, MCPP and dicamba) and insecticides (e.g., diazinon and chlorpyrifos) especially during wet event sampling.

Precipitation appears to have an influence on concentrations of pesticides in watercourses. The greatest number of pesticide detections, as well as the highest pesticide concentrations were from samples taken after rain events. There did not appear to be a seasonal pattern of inputs of pesticides into urban streams, however, the extreme variability (contributed by rainfall events) made statistical analysis difficult. This is quite different from the pattern observed in agricultural streams where the concentrations of herbicides and insecticides were higher in the late spring and early summer (USGS 1999). In this study, pesticides were frequently detected in the streams from mid-spring through mid-fall which may be associated with the practice of frequent, pre-scheduled broadcast pesticide applications commonly used in residential turf care. Several samples collected very early in the spring and late in the fall, when pesticides typically are not applied, had very few pesticide detections. This would suggest that pesticide loading to the waterbody can occur very quickly from the time of pesticide application and pesticide concentrations can decrease rapidly once applications cease.

On many occasions two or three pesticides were detected in the same sample. When this occurred, one insecticide and one or two herbicides were present in the same sample. The significance of multiple pesticide exposure on aquatic ecosystems is poorly understood and is an area that warrants further investigation.

In 20% of samples taken in this study, diazinon concentrations exceeded the Ontario Water Quality Objective for the Protection of Aquatic Life which was established to protect the health of aquatic organisms such as fish and invertebrates (0.08 ug/L, OME 1994), on one instance by as much as tenfold. These objectives are developed to protect the most sensitive aquatic organisms to an indefinite exposure to a chemical and have safety factors incorporated. Therefore, the impact of these diazinon concentrations (ND to 1.0 ug/L) on aquatic ecosystem health is difficult to determine. A similar study of urban waterways in California found concentrations of diazinon ranging from 0.26 to 1.0 ug/L (Bailey et al., 2000). Creek water was found to be lethal to water fleas (*Ceriodaphnia dubia*) in laboratory tests. The authors performed a Toxicity Identification Evaluation(TIE) and determined that diazinon was the cause of the toxicity. The authors suggest that since *Ceriodaphnia* can be considered as a surrogate for important organisms at the bottom of the food web, there may be an ecological impact at concentrations observed in the waterway. On the other hand, Giddings et al. (1999) reported that the lowest concentration of diazinon to cause an adverse ecological effect in microcosm studies (small scale experimental ecosystems) was 8.4 ug/L. Since the highest concentrations found in this study were almost ten times lower than the value reported by Giddings et al. (1999), it would appear that the concentrations of diazinon found in Toronto watersheds are not likely to have an adverse effect on the ecosystem.

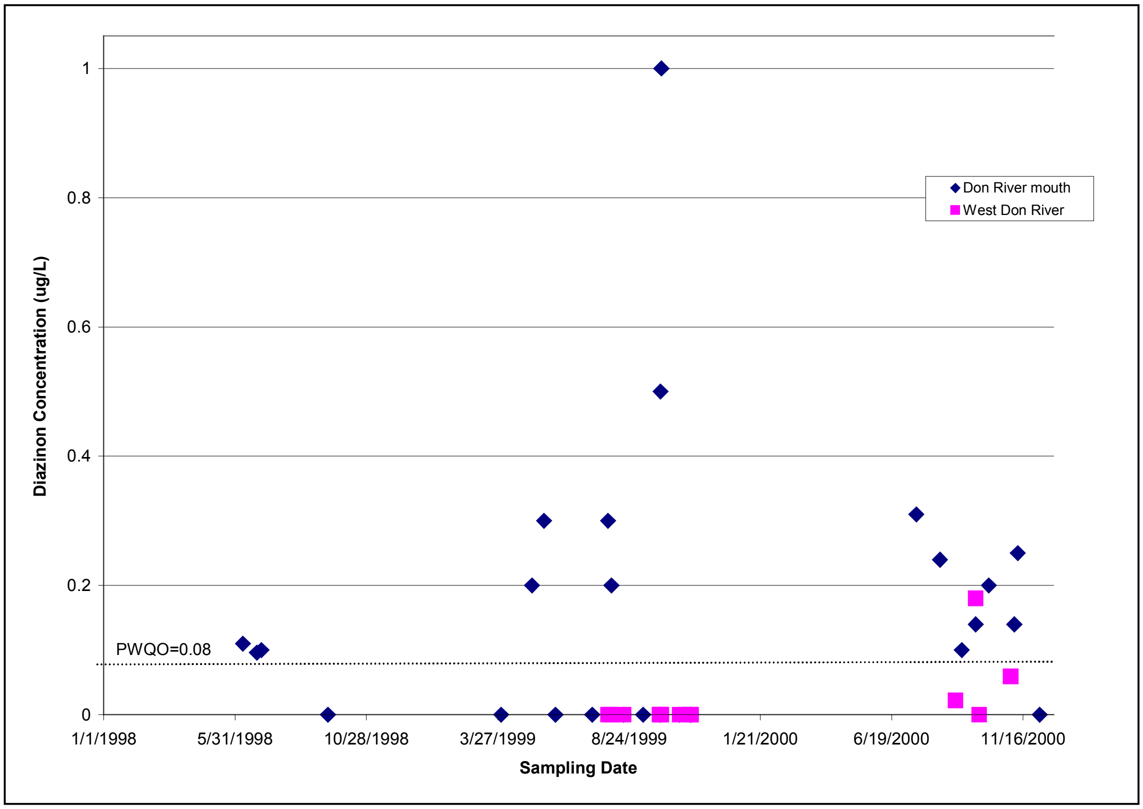

Figure 9: Diazinon Concentrations in the Don River Watershed

In general, diazinon concentrations were higher in the Don River watershed than in the Humber River watershed. As well, concentrations were generally higher at the mouths of both rivers than nearer the headwaters. As the Don River watershed is more urbanized than the Humber River watershed, and the lower reaches of both rivers are more urbanized than above, the data suggests that urban inputs of diazinon are the cause of contamination. In addition, concentrations of diazinon were often higher in samples taken during precipitation events, suggesting that surface run-off occurs quickly after the onset of rainfall.

In a monitoring survey of in use pesticides in surface waters of the Great Lakes, diazinon was not detected in the open waters of Lake Ontario (L'Italien and Struger 2001). However, the authors reported that diazinon was detected at very low concentrations (< 0.045 ug/L) in surface waters of Lake Erie.

In Ontario, diazinon applied in urban areas would primarily be used for lawn insect control. The other compounds detected (MCPP, dicamba, and 2,4-D) in this study are commonly used in urban areas for the control of weeds on lawns. However, a number of agricultural pesticides such as atrazine and metolachlor were detected at the mouths of these rivers, which suggests that agricultural inputs may alter surface water quality far downstream from where they were applied.

Hoffman et al. (2000) suggest that most pesticide inputs to urban surface waters are a result of run-off from the application of pesticides to impermeable surfaces such as parking lots, sidewalks, driveways and patios from spray drift, aerial application or misdirected application. They suggest very little run-off occurs from well-maintained grass, even during heavy rain. Thus, encouraging professional applicators and homeowners to use more caution when applying turf pesticides may help reduce the amount of pesticides in urban waterways.

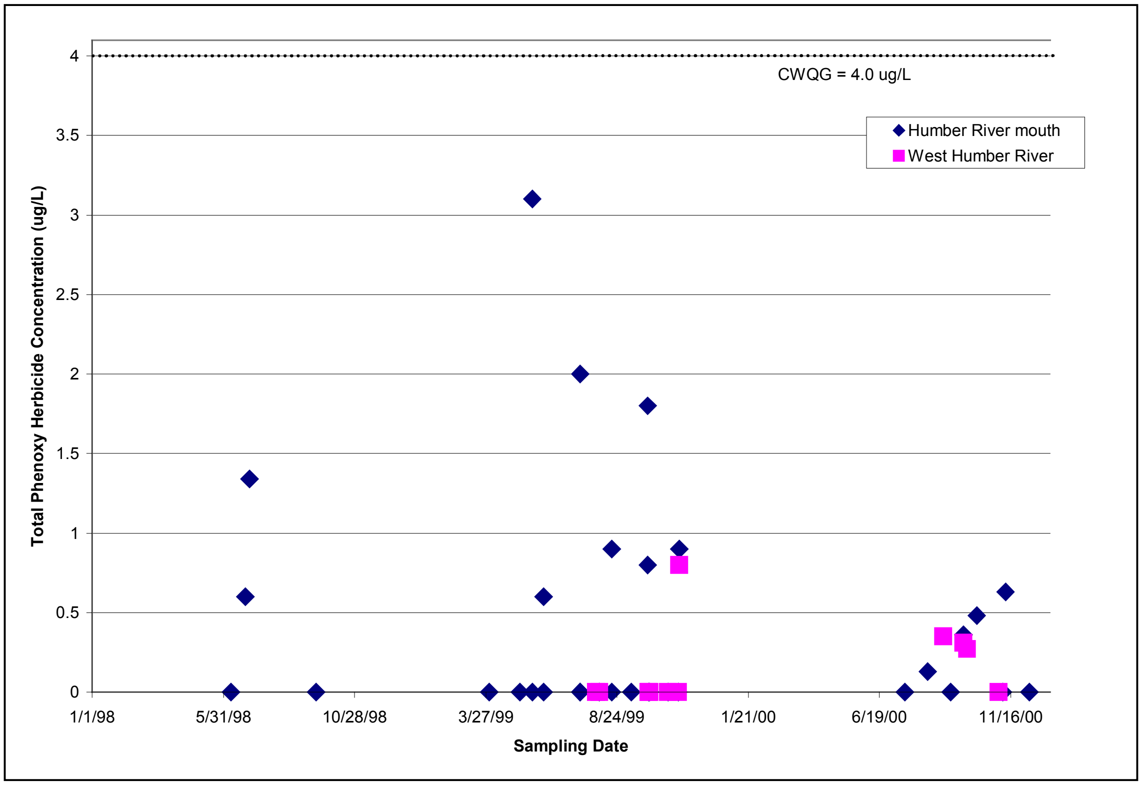

Figure 10: Total Phenoxy Herbicide Concentrations in the Humber River Watershed

In addition, a reduction in urban pesticide use, through the promotion of Integrated Pest Management (IPM) methods may lead to improved water quality. IPM is a decision making process which uses a variety of techniques, including cultural, mechanical and biological, along with pesticides, to suppress pest populations. An IPM approach emphasizes pest prevention and includes pest identification and monitoring and the use of appropriate pest management methods to reduce the reliance on pesticides. In an IPM program, treatments are only applied when needed, based on monitoring of the pest populations, in contrast to regularly scheduled applications or "calendar" sprays (Adams and Gilkeson, 1999).

The pesticide found most often in exceedence of water quality guidelines was diazinon. In December 2000, the Pest Management Regulatory Agency (PMRA) of Health Canada, which is responsible for registering pesticides for sale and use in Canada, announced the result of their re-evaluation of domestic/urban uses of diazinon products (See PMRA Re-evaluation Note REV2000-08). The PMRA has decided to restrict the domestic uses of diazinon and with the agreement of the Canadian registrants, phase-out residential turf uses of diazinon. The amount of diazinon available for sale will be reduced by 25% in 2002 and by 50% in 2003. Indoor use products will no longer be available after 2002. Outdoor use products for homeowners will be taken off the market at the end of 2003, while commercial lawncare product sales will end after 2004. Use of the products will still be allowed for one year after the end of sales. In addition, other lawn care pesticides are also being re-evaluated for their environmental and health effects by PMRA. The results of this study have been provided to the PMRA for their re-evaluation of lawncare pesticides. As the urban use of diazinon decreases, it is expected that concentrations in surface waters would also decrease over the next three to five years.

There are few registered pesticides to replace diazinon for the control of residential turf insects. Residential use of the other commonly used turf insecticide, chlorpyrifos (Dursban), ended as of December, 2001. Imidacloprid (Merit ®) is a recently introduced pesticide for the control of certain turf insects (as well as other agricultural uses) but must only be applied by licensed applicators (i.e., not available to homeowners), and must be applied at certain times of the year. It is reasonable to expect that as the use of diazinon and chlorpyrifos declines, there would be an increase in the use of imidacloprid, possibly resulting in its

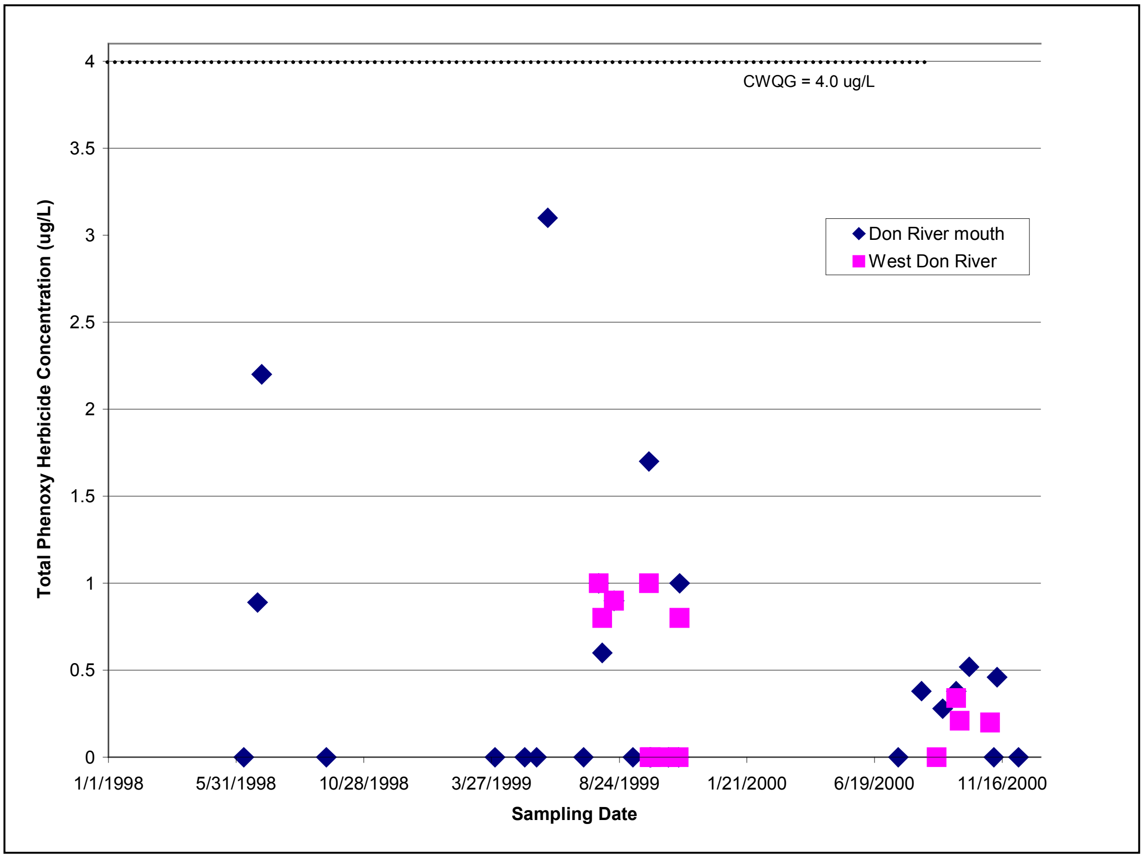

Figure 11: Total Phenoxy Herbicide Concentrations in the Don River Watershed

detection in urban waterways. Samples taken in 2000 were analyzed for imidacloprid, but there were no detections.

This study suggests that the residential use of pesticides likely contributes to pesticide concentrations in urban watersheds. It may be that the quality of these urban waterways would benefit through a reduced reliance on pesticides by homeowners and licensed applicators, possibly achieved through education and awareness on alternative methods of pest control. This change in practice would reduce the nonpoint sources of pesticides and fertilizer inputs from urban lawns. The environmental impact associated with these concentrations is currently unclear, as water quality guidelines for the protection of aquatic life are exceeded quite infrequently. Sampling of these streams continued in 2001, with emphasis on collecting surface water samples on a monthly basis for the entire use season (April through November), and to further investigate the influence of precipitation. A final report on this study is in preparation, and the authors can be contacted for this report upon its publication.

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Appendix 1. List of pesticides analyzed in 1998-2000.

2,4-D	*dithiopyr	procymidone
2,4-DB	EPN	profenofos
2,4-DP	EPTC	promethryn
alachlor	ethalfluralin	prometon
ametryn	ethion	propanil
atrazine	ethoprophos	propargite
azinphos-ethyl	etridiazole	propazine
azinphos-methyl	etrimfos	propiaconazole
benfluralin	fenamiphos	**propoxur**
bromacil	fenchlorophos	propyzamide
bromophos	fenitrothion	pyrazophos
bromophos-ethyl	fensulfothion	quinalophos
butylyate	fenthion	ridomil
carbofuran	fonofos	simazine
carbophenothion	***glyphosate and AMPA(2000)**	sultotep
carboxin	hexazinone	tebuthiuron
chlorfenvinphos(cis)	***imidacloprid**	terbacil
chlorfenvinphos(trans)	iodophenphos	terbufos
chlormephos	iprodione	terbutyrn
chlorobromuron	isofenphos	terbutylazine
chlorpyrifos	leptophos	tetrachlovinphos
chlorpyrifos-methyl	**malathion**	tolyfluancid
CIPC	**MCPA**	triadimefon
clomazone	MCPB	triallate
coumaphos	**MCPP**	trifluralin
crotoxyphos	methidathion	vernolate
crufomate	methoprotryn	vinclozlyn
cyanazine	methyltrithion	
cyanophos	metolachlor	**aldrin
cycloate	metribuzin	**alpha,beta, and delta BHC
cyprazine	mevinphos(cis)	**captafol
dementon-O	mevinphos(trans)	**captan
dementon-S	monocrotophos	**chlorbenside
desmethyl pirimicarb	myclobutanil	**cis and trans chlordane
diallate-1	nitralin	**chlorthal-dimethyl
diallate-2	nitrofen	**chlorothalonil
diazinon	oxycarboxin	**cypermethrin
dicamba	parathion	**DDD-o,p and DDD-p,p'
dichobenil	parathion-methyl	**DDE-o,p and DDE-p,p'
dichlofluanid	paroxon	**DDT-o,p and DDT-p,p'
dichloran	PCP	**deltamethrin
dichlorvos	pebulate	**dicofol
dicrotophos	pendimethalin	**endosulfan sulphate
dimethoate	phorate	**endosulfan-I and II
dimethoate-oxon	phosalone	**folpet
dinitramine	phosmet	**heptachlor and H. epoxide
dioxathion	phosphamidon	**lindane
diphenamid	pirimicarb	**mirex
diphenylamine	pirimiphos-ethyl	**cis and trans permethrin
disulfoton	pirimiphos-methyl	****quintozene**

* analyzed in 2000 only
** analyzed in 1998 and 1999 only
Common urban lawncare pesticides in bold